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Vincent Barbe, Maylise Nastar

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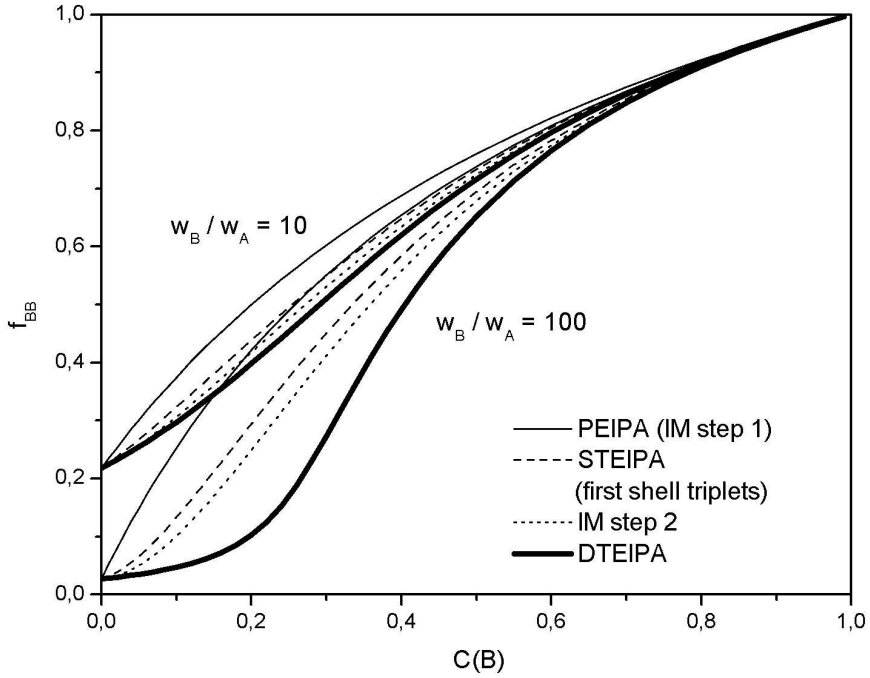

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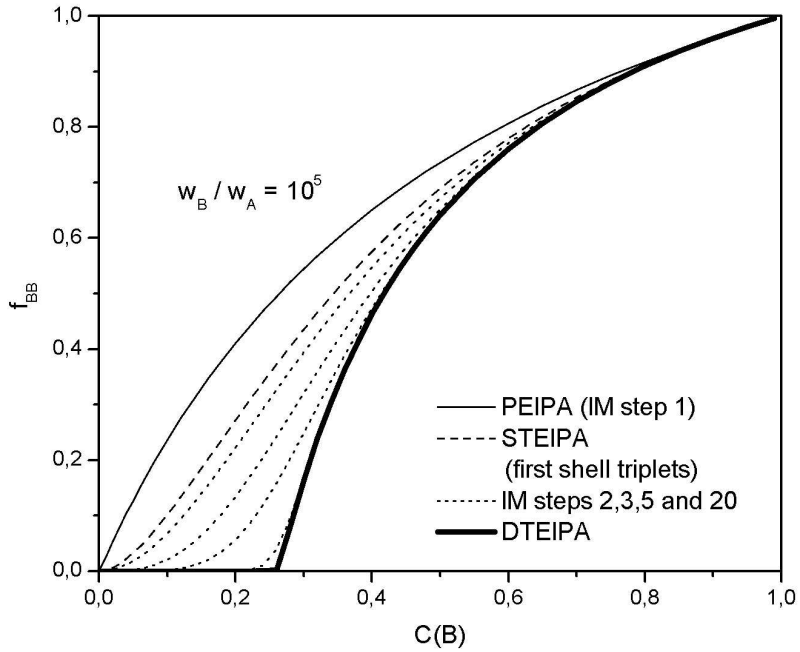

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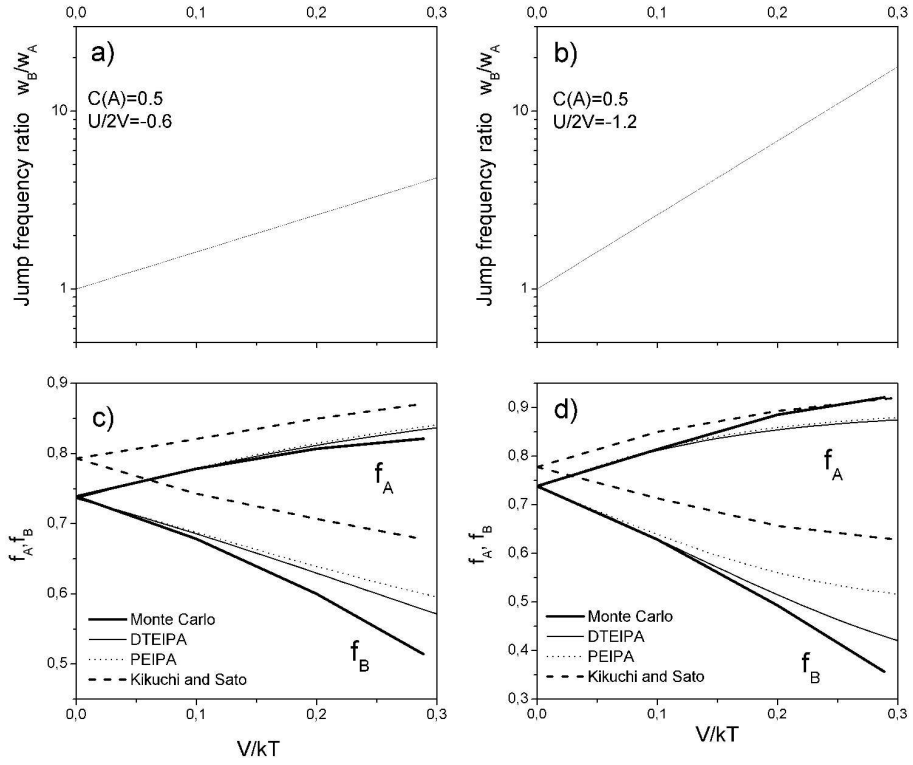

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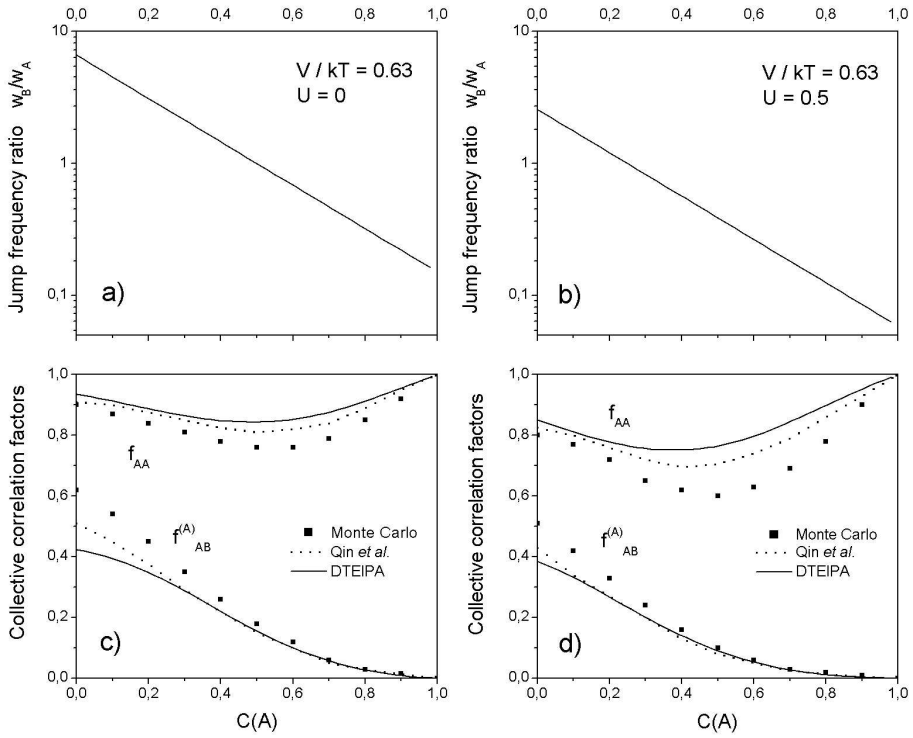

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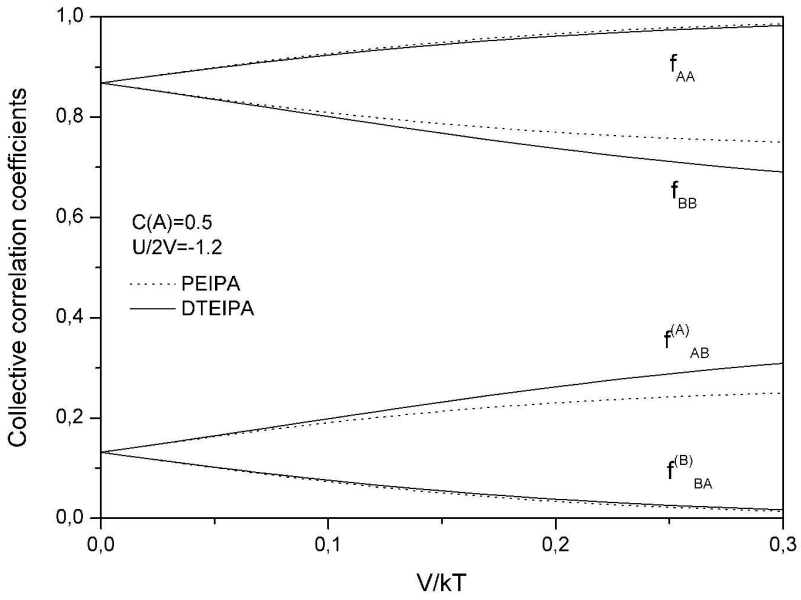

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A self-consistent mean field calculation of the phenomenological coefficients in a multicomponent alloy with high jump frequency ratios

V. Barbe*, M. Nastar
Service de Recherches en Métallurgie Physique, CEA/Saclay,
91191 Gif-sur-Yvette Cedex, France.

Abstract

We present an improvement of the self-consistent mean field (SCMF) approximation of the L_{ij} which extends its applications to alloys presenting high jump frequency ratios. The theory uses a vacancy-atom exchange model which depends on temperature and local composition through thermodynamic and kinetic parameters. Kinetic correlations due to the vacancy mechanism are represented by a time dependent effective Hamiltonian. In the case of high jump frequency ratios it is shown that long return paths of the vacancy need to be considered, which is shown to be equivalent to introduce many-body long-range effective interactions. We compare this theory to existing formalisms and Monte Carlo simulations for systems both without and with atomic interactions.

*Author for correspondence. Email : vincent.barbe@cea.fr.

1 Introduction

A general method providing with an analytical expression of the phenomenological coefficients L_{ij} of an alloy from an atomic description of the single jumps is still missing, although it is a crucial step to build a predictive model of matter transport. Numerical approaches like Monte Carlo simulations also proved their efficiency in simple models of non-interacting alloys [1, 2, 3] as well as in interacting alloys [4, 5, 6] : however the achievement of a predictive model by these methods is limited to short ranges of composition and temperature. Besides, diffusion experiments are usually performed at high temperature and for a few compositions, and only some of the total set of the transport coefficients characterizing the diffusion properties of an alloy are measured (see for example Belova and Murch [7, 8]). An extrapolation of the data to another range of temperature and composition is possible only if the obtained information completed by thermodynamic data allows to adjust an atomic diffusion model, as done by Grandjean, Bellon and Martin [9] in the Ni-Cu system with a simplified diffusion model. On the other hand ab initio calculations are now able to compute atomic jump frequencies, although mainly in dilute alloys [10, 11, 12].

The difficulty of evaluating the L_{ij} comes from the many-body nature of the difusion problem [13]. In addition to the correlation between sites due to the thermodynamic interactions between the chemical species, one needs to consider the kinetic couplings produced by the vacancy diffusion mechanism. These complex kinetic couplings can be strong even in a non-interacting alloy : in the case of an infinite jump frequency ratio they lead to the so-called percolation limit (the concentration where f_B becomes zero if B is the infinitely 'rapid' species). These effects are included in the random lattice gas theories from Manning [14, 15] to the more recent developments by Tahir-Kheli and Elliott [16], Holdsworth and Elliott [17] and eventually to the most efficient model of Moleko, Allnatt and Allnatt [18], but they are introduced by hand in diffusion models of interacting alloys. Inspired by the Manning method they are based on a tagging process of the atoms. The difficulty introduced by

the thermodynamic interactions lies in the non-random relative positions of the chemical species, as well as jump frequencies depending on the surroundings of the exchanging atom-vacancy pair. Apart from the SCMF theory, existing models treat both aspects using the jump frequency model of the Path Probability Method (see for example the review by Akbar [19]). Kikuchi and Sato [20, 21, 22] derived approximate expressions for the correlation coefficients, while the model of Stolwijk [23] was verified to be in excellent agreement with Monte Carlo simulations in bcc binary alloys, but these methods do not provide with the whole set of the phenomenological coefficients, while the later model of Qin, Allnatt and Allnatt [24] is, on the contrary, limited to the Onsager matrix of an interacting binary alloy and was not extended to the case of a tracer in a binary alloy.

The SCMF theory developed by Nastar, Dobretsov and Martin [25, 26, 27] starts from a more recent atomic diffusion model introduced by Martin [28] and extended by Nastar *et al.* [29], Athenes and Bellon [30] and Le Bouar and Soisson [31] including a variation of the saddle point energy as well as equilibrium energy with the surrounding nearest neighbours (nn) of the exchanging atom-vacancy pair. This theory leads to a complete Onsager matrix in a multicomponent system : matter fluxes are evaluated under gradients of chemical potential, and correlations due to the vacancy mechanism are described by a time dependent effective Hamiltonian. Until now only pair effective interactions were considered, which restricted the SCMF applications to alloys with limited jump frequency ratios (between 0.1 and 10 typically). The present study aims at introducing n-body interactions ($n > 2$) in order to describe more accurately the diffusion in alloys with high jump frequency ratios as far as the percolation limit.

In section II the effective Hamiltonian and its associated non-equilibrium distribution function P are presented. Kinetic equations are derived from a Master Equation applied to P. A first extension considering pair and triplet effective interactions (section III) makes the link between the vacancy return paths and the accuracy of the predicted L_{ij}. This section presents also another more efficient

derivation, based on a decoupling scheme proposed by Moleko, Allnatt and Allnatt [18] to account for all the return paths of the vacancy. In opposition to the random lattice gas theories, the SCMF theory provides with an expression of effective jump frequencies with respect to the microscopic parameters of the diffusion model. Section IV compares the SCMF results with the previous available theories and Monte Carlo simulations, and proposes a new interpretation of the Moleko *et al.* decoupling scheme in terms of an iterative method related directly to the vacancy paths. A more detailed review of the existing models in an interacting alloy is also included.

2 The SCMF theory

2.1 Non-equilibrium distribution

We consider a system of atoms and vacancies distributed on the N_s sites of a rigid lattice. A configuration $\mathbf{n}$ of the system is described by the occupation numbers $\{n_1^\alpha, n_1^\beta, \dots n_1^V, n_2^\alpha, n_2^\beta \dots\}$ where n_i^α is equal to 1 when the site i is occupied by the species α. The atomic interactions contribute to the configurational Hamiltonian $\widehat{H}^*$ as :

$$\widehat{H} = \frac{1}{2!} \sum_{i,j,A,B} V_{ij}^{AB} n_i^A n_j^B + \frac{1}{3!} \sum_{i,j,k,A,B,C} V_{ijk}^{ABC}(t) n_i^A n_j^B n_k^C + \dots \tag{1}$$

where the sums run over all species, including vacancies. At equilibrium, the probability of one configuration $\mathbf{n}$ is

$$\widehat{P}_0 = \exp\left[\beta(\Omega + \sum_{\alpha,i} \mu_\alpha n_i^\alpha - \widehat{H})\right]. \tag{2}$$

The quantity $\beta = 1/k_B T$ is the reciprocal temperature, Ω is the grand canonical potential which guarantees the relationship $\sum_{\mathbf{n}} \widehat{P}_0(\mathbf{n}) = 1$ and μ_α is the chemical potential of the species α relative to vacancies, that is the difference between the chemical potential of α and the one of vacancies. This formulation ensures that all chemical potentials μ_α are independent.

*Throughout this section, quantities which are a function of the configuration $\mathbf{n}$ will be marked by the 'hat' sign : $\widehat{H}$ stands for $H(\mathbf{n})$. Moreover, the species indexes are noted in capital letters $A, B, \dots$ when the sum includes the vacancies, and in greek caracters $\alpha, \beta, \dots$ when the sum runs over chemical species only.

Out of equilibrium, we follow Vaks' formalism [32] and define the new probability of a configuration $\mathbf{n}$ by the product of an equilibrium and a non-equilibrium part :

$$\widehat{P}(\mathbf{n},t) = \widehat{P}_0(\mathbf{n})\widehat{P}_1(\mathbf{n},t) \tag{3}$$

where the non-equilibrium contribution has the characteristic form :

$$\widehat{P}_1(\mathbf{n},t) = \exp\left[\beta\left(\delta\Omega(t) + \sum_{\alpha,i}\delta\mu_i^\alpha(t)n_i^\alpha - \hat{h}(t)\right)\right] \tag{4}$$

Following Vaks [33], in addition to the corrections to the chemical potentials and to the grand canonical potential due to non-equilibrium, we have introduced an unknown time-dependent function which will express a new set of correlations between the occupation numbers. This function $\hat{h}(t)$ is chosen to have the form of an Hamiltonian as a function of the occupation numbers and will be called *effective Hamiltonian* :

$$\hat{h}(t) = \frac{1}{2!}\sum_{i,j,\alpha,\beta} v_{ij}^{\alpha\beta}(t)n_i^\alpha n_j^\beta + \frac{1}{3!}\sum_{i,j,k,\alpha,\beta,\gamma} v_{ijk}^{\alpha\beta\gamma}(t)n_i^\alpha n_j^\beta n_k^\gamma + \dots. \tag{5}$$

The unknown time-dependent functions $v_{ij\dots}^{\alpha\beta\dots}$ are called for convenience *effective interactions* although their physical meaning is in no way comparable to the configurational interactions $V_{ij\dots}^{\alpha\beta\dots}$.

2.2 Kinetic model for the vacancy mechanism

The unknown effective interactions will be related to the transport coefficients of the system by modelling its kinetic behaviour. Following Vaks [33], we use the Master Equation :

$$\frac{d\widehat{P}(\mathbf{n},t)}{dt} = \sum_{\tilde{\mathbf{n}}}\Big[\widehat{W}(\tilde{\mathbf{n}}\to\mathbf{n})\widehat{P}(\tilde{\mathbf{n}},t) - \widehat{W}(\mathbf{n}\to\tilde{\mathbf{n}})\widehat{P}(\mathbf{n},t)\Big], \tag{6}$$

where $\widehat{W}(\mathbf{n}\to\tilde{\mathbf{n}})$ is the probability of the transition from the configuration $\mathbf{n}$ to the configuration $\tilde{\mathbf{n}}$ per time unit. In the case of the vacancy mechanism, we assume that a transition from one configuration to another is composed of only one exchange between an atom and a vacancy on a nearest neighbour (nn) site. The probability of this exchange per time unit is :

$$\widehat{W}(\mathbf{n}\to\tilde{\mathbf{n}}) = n_i^\alpha n_j^v \widehat{w}_{ij}^{\alpha v}(\mathbf{n}). \tag{7}$$

In the case of an interacting alloy, the exchange frequency $\widehat{w}_{ij}^{\alpha v}(\mathbf{n})$ has the classical thermally activated form (see [25]) :

$$\widehat{w}_{ij}^{\alpha v} = \gamma_{ij}\gamma_{\alpha} \exp\left[-\beta\left(\widehat{E}_{(s)} - \widehat{H}\right)\right] \tag{8}$$

Here γ_{ij} is a factor equal to 1 if i and j are nn and to zero otherwise, γ_{α} is an attempt frequency which is assumed to depend only on the exchanging atomic species, and the term in the exponential is the 'migration enthalpy' of the atomic exchange, that is the difference between the energy of the system in the initial configuration and when the jumping atom is at the saddle point between i and j. When considering a single atomic jump, only the contribution of the jumping atom α to the saddle point energy of the system has to be taken into account. We shall assume that this contribution $\widehat{E}_{(s)}^{\alpha}$ depends at the same time on the jumping species and on the surrounding atoms and express it in terms of pair interactions :

$$\widehat{E}_{(s)}^{\alpha} = \sum_{\sigma, k\neq i,j} V_{(s)k}^{\alpha\sigma} n_k^{\sigma} \tag{9}$$

As neither site i nor j are effectively occupied when the jumping atom is at the saddle point (s), the sum must run only on all other sites.

Consequently, one can write equation (7) accounting for the properties of the occupation numbers :

$$n_i^{\alpha} n_j^{v} \widehat{w}_{ij}^{\alpha v}(\mathbf{n}) = n_i^{\alpha} n_j^{v} \exp\left[-\beta\left(\widehat{E}_{(s)}^{\alpha} - \widehat{H}_i^{\alpha} - \widehat{H}_j^{v} + \widehat{H}_{ij}^{\alpha v}\right)\right], \tag{10}$$

where $\widehat{H}_i^{\alpha}$ is the partial derivative of $\widehat{H}$ with respect to the occupation number n_i^{α}. The last three terms correspond to the interacting bonds broken by the exchanging species in order to leave their initial position.

2.3 System of kinetic equations in the point approximation

For the calculation of the transport coefficients, we consider now the particular case of a system out of equilibrium, with the following conditions :

- The system is near an homogeneous equilibrium state, so that the non-equilibrium quantities are next to zero.
- Thanks to suitable boundary conditions, the driving force is an homogeneous chemical potential gradient.
- The system is assumed to be in steady state.

In these conditions, we solve the Master equation in order to calculate the unknown effective interactions.

We start by recalling an important result of Nastar *el al.* [25] regarding the thermodynamic averages within the framework of point approximation, also called Bragg-Williams approximation. **This approximation states that equilibrium averages of a product of occupation numbers of different sites can be decoupled as :**

$$\langle n_i^\alpha n_j^\beta \ldots \rangle^{(0)} = \langle n_i^\alpha \rangle^{(0)} \langle n_j^\beta \rangle^{(0)} \ldots . \tag{11}$$

Together with the detailed balance, one proves that the equilibrium averages of quantities of the type of equation (10) make appear mean exchange frequencies ω_α which depend only on the species of the jumping atom. This property was proven in Appendix A of [25] assuming that the saddle point energies were independent of the configuration and that the thermodynamic interactions involving vacancies were put to zero. We generalize this result in Appendix A to non-zero atom-vacancy interactions and a saddle point energy expressed in terms of pair interactions. Within this context the thermodynamic average of equation (10) can be written as :

$$\langle n_i^\alpha n_j^v \widehat{w}_{ij}^{\alpha v} \rangle = \gamma_{ij} \omega_\alpha \frac{c_\alpha}{c_v} \langle n_i^v n_j^v \rangle. \tag{12}$$

Assuming that the configuration Hamiltonian and the saddle point energy are expressed only in terms of nn pair interactions, the average frequency ω_α has the form :

$$\omega_\alpha = \gamma_\alpha \exp\left[-\beta\left(z'\sum_\sigma V^{(s)}_{\alpha\sigma}c_\sigma - z(\sum_\sigma V_{\alpha\sigma}c_\sigma - V_{\alpha v}c_v)\right)\right], \tag{13}$$

where z is the coordination number of the system and z' is the number of nn at the saddle point position ($z' = 4$ in the fcc structure, $z' = 6$ in bcc).

The last step of the SCMF method is to solve the Master equation. Instead of searching $\widehat{P}$ as a solution of the Master equation, we define it by its moments $\langle n_i^\alpha\rangle$, $\langle n_i^\alpha n_j^\beta\rangle$, that we name *n-point moments*. The kinetic equations of the type of equation (6) is applied to those moments. With help of equation (13), it comes

$$\begin{aligned}\frac{d\langle n_i^\alpha n_j^\beta n_k^\gamma \ldots\rangle}{dt} &= \sum_{s\neq i\neq j\neq\ldots}\langle n_j^\beta n_k^\gamma \ldots (n_s^\alpha n_i^v \hat{w}_{si}^{\alpha v} - n_i^\alpha n_s^v \hat{w}_{is}^{\alpha v})\rangle + \\ &\sum_{s\neq i\neq j\neq\ldots}\langle n_i^\alpha n_k^\gamma \ldots (n_s^\beta n_j^v \hat{w}_{sj}^{\beta v} - n_j^\beta n_s^v \hat{w}_{js}^{\beta v})\rangle + \ldots\end{aligned} \tag{14}$$

After linearization with respect to the terms $\beta(\delta\mu_i^\alpha - \delta\mu_s^\alpha)$ and $\beta\hat{h}_s^\alpha$ and with help of equation (12), one can write the latter equation as a function of the mean exchange frequencies ω_α and of the non-equilibrium quantities :

$$\begin{aligned}\frac{d\langle n_i^\alpha n_j^\beta n_k^\gamma \ldots\rangle}{dt} &= \beta\omega_\alpha\frac{c_\alpha}{c_v}\sum_{s\neq i\neq j\neq\ldots}\gamma_{is}\langle n_j^\beta n_k^\gamma \ldots n_s^v n_i^v(\delta\mu_s^\alpha - \delta\mu_i^\alpha - \hat{h}_s^\alpha + \hat{h}_i^\alpha)\rangle^{(0)} + \\ &\beta\omega_\beta\frac{c_\beta}{c_v}\sum_{s\neq i\neq j\neq\ldots}\gamma_{js}\langle n_i^\alpha n_k^\gamma \ldots n_s^v n_j^v(\delta\mu_s^\beta - \delta\mu_j^\beta - \hat{h}_s^\beta + \hat{h}_j^\beta)\rangle^{(0)} + \ldots,\end{aligned} \tag{15}$$

where $^{(0)}$ means averaging over the equilibrium distribution function P_0, and $\hat{h}_s^\alpha$ is the partial derivative of $\hat{h}$ with respect to the occupation number n_s^α. Furthermore, the difference $\beta(\delta\mu_i^\alpha - \delta\mu_s^\alpha)$ is equal to the difference of the total chemical potentials since the equilibrium contribution to the difference is equal to zero. The number of n-point moments to account for depends on the truncation of the effective Hamiltonian $\hat{h}$: if restricted to nn pair effective interactions, it is sufficient to solve the kinetic equations of all nn 2-point moments.

2.4 Transport coefficients and correlation effects

The link with the transport coefficients is based on the time derivative of the one-point moment $\langle n_i^\alpha \rangle$. This moment can also be defined as an equilibrium local concentration c_i^α. Applying equation (15), one recognizes the equation of matter conservation

$$\frac{dc_i^\alpha}{dt} = -\sum_{j \neq i} J_{i \to j}^\alpha, \tag{16}$$

where the flux of atoms α from site i to site j is identified as :

$$J_{i \to j}^\alpha = -\beta \omega_\alpha \frac{c_\alpha}{c_V} \gamma_{ij} \langle n_i^V n_j^V (\mu_j^\alpha - \mu_i^\alpha - \hat{h}_j^\alpha + \hat{h}_i^\alpha) \rangle. \tag{17}$$

As the system of equations (15) is linear in the differences between sites of the chemical potentials, the effective interactions that are deduced from (15) are a linear combination of gradients of chemical potentials. We can then define the transport coefficients of the system regarding the species α as :

$$L_{\alpha\alpha}^{(0)} = \beta \omega_\alpha c_\alpha c_V \tag{18}$$

$$\langle n_i^V n_j^V (\hat{h}_j^\alpha - \hat{h}_i^\alpha) \rangle = c_V^2 \sum_\sigma (\delta_{\alpha\sigma} - f_{\alpha\sigma}^{(\alpha)})(\mu_j^\alpha - \mu_i^\alpha), \tag{19}$$

the latter equation being valid only when the sites i and j are nearest neighbours. **Here the L and f coefficients follow the usual definitions : the superscript $L_{ii}^{(0)}$ stands for the uncorrelated part of the Onsager coefficient, and the correlation coefficients f are defined as :**

$$f_{ij}^{(i)} = \frac{L_{ij}}{L_{ii}^{(0)}}, \tag{20}$$

where the superscript is omitted if i equals j.

As we can see, the uncorrelated part of the transport coefficients is obtained without the help of the effective Hamiltonian. Correlation effects (off-diagonal terms of the L-matrix) appear only when the effective Hamiltonian is taken into account at least until the pair effective interactions, and they are defined by the linear relation between the partial derivatives of $\hat{h}$ and the driving forces $(\mu_j^\alpha - \mu_i^\alpha)$.

3 Application of the SCMF model to strongly correlated systems

The calculation of the transport coefficients of an interacting alloy by the SCMF method was derived by Nastar *el al.* [25] using two main approximations : firstly, the point approximation in the calculation of equilibrium thermodynamic averages, and secondly the truncation of the effective Hamiltonian to infinite-range pair interactions. The results, which we recall in the next paragraph, were very satisfactory in a binary alloy as long as the ratio of the mean exchange frequencies ω_α was between 0.1 and 10. To enhance the accuracy of the SCMF method beyond this limit, we derive the kinetic equations for an effective Hamiltonian which includes triplet effective interactions and propose a simplified treatment of these quantities to reach infinite-range interactions.

3.1 Resolution of the kinetic equations with pair effective interactions within the point approximation (PEIPA)

In this paragraph we recall the results obtained in [25]. For the thermodynamic averages, one must pay a particular attention to the following relation :

$$n_i^\alpha n_i^\beta = \delta_{\alpha\beta} n_i^\alpha \tag{21}$$

where $\delta_{\alpha\beta}$ is the Kroenecker symbol. This relation has a prior importance in the following developments of the calculation. In particular, the expression of the fluxes in equation (17) becomes :

$$\begin{aligned} J_{i\to j}^\alpha &= -\beta\omega_\alpha c_\alpha c_V^2 \gamma_{ij} \left[\mu_j^\alpha - \mu_i^\alpha - \sum_\sigma \left(v_{ij}^{\alpha\sigma} - v_{ji}^{\alpha\sigma} \right) c_\sigma \right] \\ &= -\beta\omega_\alpha c_\alpha c_V^2 \gamma_{ij} \left[\mu_j^\alpha - \mu_i^\alpha - (h_{ij}^\alpha - h_{ji}^\alpha) \right] \end{aligned} \tag{22}$$

where h_{ij}^α is the contribution to the *effective field* experienced by an atom α on a site i due to another site j. Note that the difference $(\sum_{\sigma,k} v_{ik}^{\alpha\sigma} n_k^\sigma - \sum_{\sigma,k} v_{jk}^{\alpha\sigma} n_k^\sigma)$ was eliminated since by symmetry it is equal to zero.

Equation (19) then becomes :

$$h_{ij}^{\alpha} - h_{ji}^{\alpha} = \sum_{\sigma} (\delta_{\alpha\sigma} - f_{\alpha\sigma}^{(\alpha)})(\mu_j^{\alpha} - \mu_i^{\alpha}). \tag{23}$$

To calculate the pair effective interactions, it is sufficient to consider the time derivative of the 2-point moment $\langle n_i^{\alpha} n_j^{\beta} \rangle$, or the 2-point correlator $K_{ij}^{\alpha\beta} = \langle (n_i^{\alpha} - c_i^{\alpha})(n_j^{\beta} - c_j^{\beta}) \rangle$. With help once more of the detailed balance, we find :

$$\begin{aligned} \frac{dK_{ij}^{\alpha\beta}}{dt} &= \beta\omega_{\alpha} c_V^2 c_{\alpha} c_{\beta} \sum_{s \neq j} \gamma_{is} \left(h_{sj}^{\alpha\overline{\beta}} - h_{ij}^{\alpha\overline{\beta}} \right) \\ &+ \beta\omega_{\beta} c_V^2 c_{\alpha} c_{\beta} \sum_{s \neq i} \gamma_{js} \left(h_{si}^{\beta\overline{\alpha}} - h_{ji}^{\beta\overline{\alpha}} \right) \\ &+ c_j^{\beta} J_{i \to j}^{\alpha} + c_i^{\alpha} J_{j \to i}^{\beta} \end{aligned} \tag{24}$$

where the quantity $h_{ij}^{\alpha\overline{\beta}}$ is a difference between partial effective fields defined by :

$$h_{ij}^{\alpha\overline{\beta}} = \sum_{\sigma} v_{ij}^{\alpha\sigma} c_{\sigma} - v_{ij}^{\alpha\beta} \tag{25}$$

When i and j are not nn, the flux $J_{i \to j}^{\alpha}$ is equal to zero, and the associated equations (24) can be taken into account by simply introducing a geometrical factor z^* in the corresponding nn 2-point correlator equation :

$$-\omega_{\alpha} c_{\alpha} c_{\beta} c_V^2 (z^* - 1) h_{ij}^{\alpha\overline{\beta}} - \omega_{\beta} c_{\alpha} c_{\beta} c_V^2 (z^* - 1) h_{ji}^{\beta\overline{\alpha}} + c_j^{\beta} J_{i \to j}^{\alpha} + c_i^{\alpha} J_{j \to i}^{\beta} = 0 \tag{26}$$

The factor z^* expresses the geometry of the system through the influence of long-range 2-point correlators. Its calculation leads to a simple relation with the tracer self-correlation factor f_0 in the same geometry :

$$f_0 = \frac{z^* - 1}{z^* + 1} \tag{27}$$

The final expressions for the correlation coefficients in a binary alloy AB are then given by :

$$\begin{aligned} f_{AA} &= 1 - \frac{2\omega_A c_B}{(z^* - 1)(\omega_A(1 - c_B) + \omega_B(1 - c_A)) + 2(\omega_A c_B + \omega_B c_A)} \\ f_{AB}^{(A)} &= \frac{2\omega_B c_B}{(z^* - 1)(\omega_A(1 - c_B) + \omega_B(1 - c_A)) + 2(\omega_A c_B + \omega_B c_A)} \end{aligned} \tag{28}$$

The coefficients f_{BB} and $f_{AB}^{(B)}$ are obtained by inverting indexes A and B in the latter expressions.

3.2 Truncation to triplet effective interactions (TEIPA)

In order to improve the accuracy of the model when the mean exchange frequencies are very different (for example $\omega_B/\omega_A \gg 1$), we choose to take into account the triplet effective interactions in the expression of the effective Hamiltonian $\hat{h}(t)$:

$$\hat{h}(t) = \frac{1}{2!}\sum_{i,j,\alpha,\beta} v_{ij}^{\alpha\beta}(t) n_i^\alpha n_j^\beta + \frac{1}{3!}\sum_{i,j,k,\alpha,\beta,\gamma} v_{ijk}^{\alpha\beta\gamma}(t) n_i^\alpha n_j^\beta n_k^\gamma \tag{29}$$

The flux of species α as a function of the effective interactions then becomes in the point approximation :

$$J_{i\to j}^\alpha = -\beta\omega_\alpha c_\alpha c_V^2 \gamma_{ij}\left[\mu_j^\alpha - \mu_i^\alpha - \sum_\sigma\left(v_{ij}^{\alpha\sigma} - v_{ji}^{\alpha\sigma} + \sum_{\sigma',s}(v_{ijs}^{\alpha\sigma\sigma'} - v_{jis}^{\alpha\sigma\sigma'})c_{\sigma'}\right)c_\sigma\right] \tag{30}$$

which is strictly equivalent to equation (22), given the definition of the partial effective fields h_{ij}^α. Equation (23) remains unchanged for the same reason. The calculation of the time derivative of the 2-point correlator gives rise to notable differences :

$$\begin{aligned}\frac{dK_{ij}^{\alpha\beta}}{dt} &= \beta\omega_\alpha c_V^2 c_\alpha c_\beta \sum_{s\neq j}\gamma_{is}\left(h_{sj}^{\alpha\overline{\beta}} - h_{ij}^{\alpha\overline{\beta}} - \sum_{s'\neq i,j,s}(h_{sjs'}^{\alpha\overline{\beta}} - h_{ijs'}^{\alpha\overline{\beta}})\right)\\ &\quad +\beta\omega_\beta c_V^2 c_\alpha c_\beta \sum_{s\neq i}\gamma_{js}\left(h_{si}^{\beta\overline{\alpha}} - h_{ji}^{\beta\overline{\alpha}} - \sum_{s'\neq i,j,s}(h_{sis'}^{\beta\overline{\alpha}} - h_{jis'}^{\beta\overline{\alpha}})\right)\\ &\quad +c_j^\beta J_{i\to j}^\alpha + c_i^\alpha J_{j\to i}^\beta\end{aligned} \tag{31}$$

where the partial effective fields h bear the following expressions :

$$\begin{aligned}h_{ij}^{\alpha\overline{\beta}} &= h_{ij}^\alpha - h_{ij}^{\alpha\beta}\\ &= \sum_\sigma c_\sigma\left(v_{ij}^{\alpha\sigma} + \sum_{s,\sigma'} v_{ijs}^{\alpha\sigma\sigma'}c_{\sigma'}\right) - \left(v_{ij}^{\alpha\beta} + \sum_{s,\sigma'} v_{ijs}^{\alpha\beta\sigma'}c_{\sigma'}\right)\end{aligned} \tag{32}$$

$$\begin{aligned}h_{ijs}^{\alpha\overline{\beta}} &= h_{ijs}^\alpha - h_{ijs}^{\alpha\beta}\\ &= \sum_{\sigma,\sigma'} c_\sigma c_{\sigma'} v_{ijs}^{\alpha\sigma\sigma'} - \sum_{\sigma'} c_{\sigma'} v_{ijs}^{\alpha\beta\sigma'}\end{aligned} \tag{33}$$

The basic equations $dK_{ij}^{\alpha\beta}/dt = 0$ are not sufficient to calculate the correlation effects now that we have introduced the unknown triplet effective interactions. The simplest and straightforward way

to complete the set of equations is to calculate the time-derivative of the 3-point correlators $K_{ijk}^{\alpha\beta\gamma}$. Assuming that the 4-point effective interactions are set equal to zero, their expression is :

$$\begin{aligned}\frac{dK_{ijk}^{\alpha\beta\gamma}}{dt} &= \beta\omega_\alpha c_v c_\alpha c_\beta c_\gamma \Big(\sum_{s\neq j\neq k} \gamma_{is} \left(h_{sjk}^{\alpha\overline{\beta}\overline{\gamma}} - h_{ijk}^{\alpha\overline{\beta}\overline{\gamma}} \right) - \gamma_{ij}(h_{jk\bar{i}}^{\alpha\overline{\gamma}} - h_{ik\bar{j}}^{\alpha\overline{\gamma}}) - \gamma_{ik}(h_{kj\bar{i}}^{\alpha\overline{\beta}} - h_{ij\bar{k}}^{\alpha\overline{\beta}}) \Big) \\ &+\beta\omega_\beta c_v c_\alpha c_\beta c_\gamma \Big(\sum_{s\neq i\neq k} \gamma_{js} \left(h_{sik}^{\beta\overline{\alpha}\overline{\gamma}} - h_{jik}^{\beta\overline{\alpha}\overline{\gamma}} \right) - \gamma_{ji}(h_{ik\bar{j}}^{\beta\overline{\gamma}} - h_{jk\bar{i}}^{\beta\overline{\gamma}}) - \gamma_{jk}(h_{ki\bar{j}}^{\beta\overline{\alpha}} - h_{ji\bar{k}}^{\beta\overline{\alpha}}) \Big) \\ &+\beta\omega_\gamma c_v c_\alpha c_\beta c_\gamma \Big(\sum_{s\neq i\neq j} \gamma_{ks} \left(h_{sij}^{\gamma\overline{\alpha}\overline{\beta}} - h_{kij}^{\gamma\overline{\alpha}\overline{\beta}} \right) - \gamma_{kj}(h_{ji\bar{k}}^{\gamma\overline{\alpha}} - h_{ki\bar{j}}^{\gamma\overline{\alpha}}) - \gamma_{ki}(h_{kj\bar{i}}^{\gamma\overline{\beta}} - h_{ij\bar{k}}^{\gamma\overline{\beta}}) \Big) \end{aligned} \quad (34)$$

where we have introduced more compact forms for partial effective fields :

$$h_{ijk}^{\alpha\overline{\beta}\overline{\gamma}} = h_{ijk}^{\alpha} - h_{ijk}^{\alpha\beta} - h_{ikj}^{\alpha\gamma} + h_{ijk}^{\alpha\beta\gamma} \quad (35)$$

$$h_{ij\bar{k}}^{\alpha\overline{\beta}} = h_{ij}^{\alpha} - h_{ij}^{\alpha\beta} - h_{ijk}^{\alpha} + h_{ijk}^{\alpha\beta} \quad (36)$$

3.3 A decoupling scheme

The calculation of the time derivative of all 3-point correlators implies a heavy geometrical effort and the long-range interactions do not seem to converge towards a simple physical value as for the pair interactions. As an alternative set of equations, we shall refer to the Moleko, Allnatt and Allnatt [18] decoupling scheme (MAA), that was used within the framework of the Random Lattice Gas theory to calculate the correlation coefficients in non-interacting systems. We need to express a hierarchy of 1-point, 2-point and 3-point quantities, identify a relation between the 2-point and 1-point ones and impose the same relation between the 3-point and 2-point ones. In the TEIPA formalism, the analogue of the equilibrium fluctuations are the non-equilibrium quantities $\{h^{(n)}\}$ defined by the following expressions :

$$\begin{aligned}\{h^{(1)}\}_i^\alpha &= \delta\mu_i^\alpha + \sum_{\sigma,s} v_{is}^{\alpha\sigma} c_\sigma + \sum_{\sigma,\sigma',s,s'} v_{iss'}^{\alpha\sigma\sigma'} c_\sigma c_{\sigma'} \\ \{h^{(2)}\}_{ij}^{\alpha\beta} &= v_{ij}^{\alpha\beta} + \sum_{\sigma,s} v_{ijs}^{\alpha\beta\sigma} c_\sigma \\ \{h^{(3)}\}_{ijk}^{\alpha\beta\gamma} &= v_{ijk}^{\alpha\beta\gamma}. \end{aligned} \quad (37)$$

In an isotropic cristal, symmetry considerations lead to the simplified form of the 1-point non-equilibrium function :

$$\{h^{(1)}\}_i^\alpha = \delta\mu_i^\alpha. \tag{38}$$

Equation (19) provides with a direct relationship between the 1-point and 2-point functions :

$$\sum_\sigma (\{h^{(2)}\}_{ij}^{\alpha\sigma} - \{h^{(2)}\}_{ji}^{\alpha\sigma}) c_\sigma = \sum_\sigma (\delta_{\alpha\sigma} - f_{\alpha\sigma}^{(\alpha)})(\{h^{(1)}\}_j^\sigma - \{h^{(1)}\}_i^\sigma). \tag{39}$$

This relation is strictly equivalent to the one identified in the work of Moleko *et al* [18], involving in the same way the macroscopic term $(\delta_{\alpha\sigma} - f_{\alpha\sigma}^{(\alpha)})$. As an additional set of equations, we transpose this relation to the 3-point and 2-point functions by adding to each member a given site k occupied by a given species β. The new equation states :

$$\sum_\sigma (\{h^{(3)}\}_{ijk}^{\alpha\sigma\beta} - \{h^{(3)}\}_{jik}^{\alpha\sigma\beta}) c_\sigma = \sum_\sigma (\delta_{\alpha\sigma} - f_{\alpha\sigma}^{(\alpha)})(\{h^{(2)}\}_{jk}^{\sigma\beta} - \{h^{(2)}\}_{ik}^{\sigma\beta}). \tag{40}$$

It is worth noting that equation (39) is valid only when sites i and j are nearest neighbours, as its equivalent in the MAA formalism is also valid only at the limit of infinite wavelenghts. On the contrary, the deduced relationship equation (40) is to be applied for all wavelenghts in the MAA formalism and for all (i, j) couples in ours. With help of the latter relation, one can re-write the time derivative of the 2-point correlator within a Decoupled TEIPA formalism (DTEIPA) :

$$\begin{aligned}
\frac{dK_{ij}^{\alpha\beta}}{dt} &= \beta\omega_\alpha c_V^2 c_\alpha c_\beta \sum_{s\neq j} \gamma_{is} \left(h_{sj}^{\alpha\overline{\beta}} - h_{ij}^{\alpha\overline{\beta}} - \sum_\sigma (\delta_{\alpha\sigma} - f_{\alpha\sigma}^{(\alpha)})(h_{sj}^{\sigma\overline{\beta}} - h_{ij}^{\sigma\overline{\beta}}) \right) \\
&\quad + \beta\omega_\beta c_V^2 c_\alpha c_\beta \sum_{s\neq i} \gamma_{js} \left(h_{si}^{\beta\overline{\alpha}} - h_{ji}^{\beta\overline{\alpha}} - \sum_\sigma (\delta_{\beta\sigma} - f_{\beta\sigma}^{(\alpha)})(h_{si}^{\sigma\overline{\alpha}} - h_{ji}^{\sigma\overline{\alpha}}) \right) \\
&\quad - c_j^\beta J_{i\to j}^\alpha - c_i^\alpha J_{j\to i}^\beta.
\end{aligned} \tag{41}$$

Because of the application of equation (40) to all (i, j) couples, the system can be reduced to a single equation associated with the nn correlators, except that the coordination number z is replaced by z^* as earlier. The equation to solve is of the following type :

$$-\omega_\alpha c_\alpha c_\beta c_V^2 (z^* - 1) \sum_\sigma f_{\alpha\sigma}^{(\alpha)} h_{ij}^{\sigma\overline{\beta}} - \omega_\beta c_\alpha c_\beta c_V^2 (z^* - 1) \sum f_{\beta\sigma}^{(\beta)} h_{ji}^{\sigma\overline{\alpha}} - c_j^\beta J_{i\to j}^\alpha - c_i^\alpha J_{j\to i}^\beta = 0. \tag{42}$$

In the particular case of a binary alloy, one obtains the following relations between the correlation coefficients :

$$\begin{aligned} f_{AA} &= 1 - \frac{2\omega_A c_B}{(z^*-1)((f_{AA}(1-c_B)+f_{AB}^{(A)}c_A)\omega_A + (f_{BB}(1-c_A)+f_{BA}^{(B)}c_B)\omega_B) + 2(\omega_A c_B + \omega_B c_A)} \\ f_{AB}^{(A)} &= \frac{2\omega_B c_B}{(z^*-1)((f_{AA}(1-c_B)+f_{AB}^{(A)}c_A)\omega_A + (f_{BB}(1-c_A)+f_{BA}^{(B)}c_B)\omega_B) + 2(\omega_A c_B + \omega_B c_A)} \end{aligned} \quad (43)$$

and the expression for f_{BB} and $f_{BA}^{(B)}$ are obtained by inverting A and B in the above equations. As for the approximation of pair effective interactions, we could not reach an analytical expression for the correlation coefficients in a ternary alloy ABC with three different frequencies. Nevertheless, the numerical solving of the system formed of equations (42) for all couples $(\alpha\beta)$ presents no difficulty and does not require additional geometrical calculation.

It is to notice that equation (40), which is the basis of our decoupling scheme, can also be interpreted in terms of the non-equilibrium distribution function of an alloy under a gradient of chemical potential using equations (2)-(4). Such an analysis is to be found in Appendix B of the present study.

4 Results and discussion

The particularity of the SCMF model when used in the point approximation is that an interacting alloy eventually appears like a non-interacting alloy where the species-dependent exchange frequencies depend on the composition of the system but not on the atoms surrounding the exchanging pair. Note that the same SCMF model when used in a higher statistical approximation provides with a set of exchange frequencies depending on the local environment, **although this treatment was used up to now only in the simple case of a dilute alloy** [27]. It is then straightforward to compare the results of the different approximation levels of the SCMF ([25] and this work) with the main theories available for the random lattice gas system, the formalisms of Manning [14, 15] and of Moleko *et al.* [18]. In a second part, the SCMF theory will be tested against the models of

Stolwijk [23], Kikuchi and Sato [20, 22] and Qin, Allnatt and Allnatt [24] devoted to solid solutions of interacting alloys on the basis of available Monte Carlo simulations [6, 23, 34]. **Due to the use of the point approximation without a sublattice formalism, the SCMF theory in its present versions is clearly designed for interacting alloys without long range order. Hence reference theories as well as Monte Carlo simulations by Bakker [35], Murch [4], Wang and Akbar [36] or Qin *et al.* [37] in ordered alloys shall not be adressed in this discussion. Eventually, although all previous equations are meant for a general vacancy content, all comparisons in this section will be carried out in the simple case of a binary alloy AB in the limit of small vacancy content, which is the system where most of other formalisms have been tested.**

4.1 Non-interacting alloy

In this paragraph the exchange frequencies ω_A and ω_B are taken to be concentration-independent. We introduce for convenience the reduced mean exchange frequencies $\omega = \omega_A c_A + \omega_B c_B$ and $\omega' = \omega_A c_B + \omega_B c_A$. It is then possible to write a simplified expression of the correlation factors in the PEIPA formalism

$$f_{AA} = 1 - \frac{2\omega_A c_B}{(z^*-1)\omega + 2\omega'} \quad (44)$$

$$f_{AB}^{(A)} = \frac{2\omega_B c_B}{(z^*-1)\omega + 2\omega'} \quad (45)$$

$$f_A = \frac{(z^*-1)(\omega+\omega_B)}{(z^*-1)(\omega+\omega_B) + 2\omega_A} \quad (46)$$

and in the DTEIPA formalism

$$f_{AA} = 1 - \frac{2\omega_A c_B}{(z^*-1)((f_{AA}+f_{AB}^{(A)})\omega_A c_A + (f_{BB}+f_{BA}^{(B)})\omega_B c_B) + 2\omega'} \quad (47)$$

$$f_{AB}^{(A)} = \frac{2\omega_B c_B}{(z^*-1)((f_{AA}+f_{AB}^{(A)})\omega_A c_A + (f_{BB}+f_{BA}^{(B)})\omega_B c_B) + 2\omega'} \quad (48)$$

$$f_A = \frac{(z^*-1)\omega_A(f_{AA}+f_{AB}^{(A)}+f_{AA^*}^{(A)}+f_{A^*A}^{(A^*)}-f_{A^*A^*})}{(z^*-1)\omega_A(f_{AA}+f_{AB}^{(A)}+f_{AA^*}^{(A)}+f_{A^*A}^{(A^*)}-f_{A^*A^*}) + 2\omega_A} \quad (49)$$

whereas the results in the Simple TEIPA formalism (STEIPA) are only numerical, corresponding to consider a finite number of triplet interactions.

As expected by Nastar *et al.* [25], the difference between the TEIPA and PEIPA formalisms increases with the exchange frequency ratio. When the exchange frequencies are equal (tracer in a pure metal), the PEIPA already leads to exact results, and the effective interactions beyond pair interactions are all found to be zero. Figures 1 and 2 show the predicted f_{BB} coefficient in all three approximations for exchange frequencies ratios ω_B/ω_A repectively equal to 10, 100 and 10^5 in a bcc lattice. As for the STEIPA curves, only the triplet effective interactions corresponding to 'compact' triangles, i.e. formed of two pairs of nearest neighbours, are actually calculated. Taking into account the next triplet effective interactions makes an almost undistinguishable change in the coefficient f_{BB}, even for the most correlated case. We note that, in this extreme case, only the DTEIPA predicts a percolation effect, the percolation threshold being located at the concentration $C(B) = 1 - f_0$. The other correlation coefficients are not drawn, as all three approximations (PEIPA, STEIPA and PEIPA) obey the Moleko and Allnatt [38] analytical relation :

$$\sum_j f_{ij}^{(i)} \frac{\omega_i}{\omega_j} = 1. \tag{50}$$

As a consequence, only one correlation coefficient is sufficient to describe a binary alloy. We choose to represent the coefficient f_{BB}, which exhibits the most visible discrepancies between the different theories.

When compared to other theories, the different SCMF approximations show noteworthy similarities. Namely, the analytical expressions for the collective correlation factors of the PEIPA are almost identical to the formalism of Kikuchi and Sato [20] within the framework of the path probability method, except that z^* is replaced in the latter model by the coordination number z. In the same way, the collective correlation factors of the DTEIPA correspond exactly to Manning's [15] and the MAA [18] formalisms which are known to be identical in the case of a binary alloy and very

accurate when compared with the recent Monte Carlo simulations by Belova and Murch [2, 3]. As for the tracer correlation factor, the DTEIPA equals the most accurate MAA theory. Namely, due to the similarity of the decoupling scheme, the results of both DTEIPA and MAA coincide also in the ternary alloy, as in the general multicomponent systems. To investigate the physical meaning of the effective interactions introduced by the SCMF formalism, we look at the different theories in terms of vacancy escape frequencies as introduced by Manning. Beyond Manning's model, we make a difference between the escape frequency of a vacancy when it is involved in a collective correlation factor, H^{col}, and in a tracer correlation factor, H^{tr}. The formalism in which the escape frequency is calculated will be refered to in subscript, e.g., H^{col}_{PEI} stands for H^{col}_{PEIPA}. The analytical expressions of those quantities in the SCMF formalism are to be seen in equations (44)-(49) which all exhibit the characteristic form :

$$f_{AA} = 1 - \frac{2\omega_A c_B}{H^{col} + 2\omega'} \quad (51)$$

$$f_A = \frac{H^{tr}}{H^{tr} + 2\omega_A} \quad (52)$$

The value of $H^{col}_{PEI} = (z^*-1)\omega$ with $z^* = (1+f_0)/(1-f_0)$ corresponds to a vacancy moving through uncorrelated jumps in a one-component system with an exchange frequency ω. As a consequence, only the first return jump of a vacancy is precisely accounted for in the PEIPA for the calculation of the collective correlation effects. In the DTEIPA, $H^{col}_{DTEI} = (z^*-1)((f_{AA}+f^{(A)}_{AB})\omega_A c_A + (f_{BB}+f^{(B)}_{BA})\omega_B c_B)$ expresses the main physical assumption of Manning, who expressed the escape frequency as a function of the macroscopic correlation coefficients : all possible paths for the return of the vacancy are then taken into account whereas one considers only the escape frequency as a macroscopic quantity. According to the Monte Carlo simulations which show the superiority of the MAA formalism, Manning's assumption was not sufficient in ternary systems. As an application, the calculation of H^{tr} needs a further improvement which is achieved by the DTEIPA or the MAA theory : both formalisms take into account the correlations due to the tracer in the exchange frequency (three last terms of

H^{tr}_{DTEI} in equation (49)).

One last result will unify those remarks and enlight the link between the different approximations of the SCMF and the return path of the vacancy which is actually taken into account. Following the results of the DTEIPA, we express the collective correlation coefficients as

$$f_{AA} = 1 - \frac{2\omega_A c_B}{(z^*-1)((\tilde{f}_{AA}+\tilde{f}^{(A)}_{AB})\omega_A c_A + (\tilde{f}_{BB}+\tilde{f}^{(B)}_{BA})\omega_B c_B) + 2\omega'}, \quad (53)$$

$$f^{(A)}_{AB} = \frac{2\omega_B c_B}{(z^*-1)((\tilde{f}_{AA}+\tilde{f}^{(A)}_{AB})\omega_A c_A + (\tilde{f}_{BB}+\tilde{f}^{(B)}_{BA})\omega_B c_B) + 2\omega'}, \quad (54)$$

where the $\tilde{f}_{ij}$ are the correlation factors obtained in the PEIPA formalism (equations (44)-(45)). This expression can be read from two different points of view. On the one hand, this calculation is the second iteration in calculating 'by hand' the correlation coefficients in the DTEIPA by an iterative method (IM) : the zeroth iteration bears $f_{AA} = 1$ and $f^A_{AB} = 0$, the first iteration gives the PEIPA results, and at each step the correlation factors are calculated using equation (53) where the $\tilde{f}$ are the result of the preceeding step. On the other hand, let us observe the infered escape frequency of the 'second interation' $H^{col} = (z^*-1)((\tilde{f}_{AA}+\tilde{f}^{(A)}_{AB})\omega_A c_A + (\tilde{f}_{BB}+\tilde{f}^{(B)}_{BA})\omega_B c_B)$. As in Manning's spirit, this frequency includes all return paths of the vacancy through the macroscopic correlation coefficients ; but those coefficients themselves express that, after a first jump, the vacancy migration is uncorrelated in an average one-component system. Consequently, the 'second-iteration' escape frequency may be interpreted as the precise accounting for two successive jumps. Numerically, the obtained results are in good agreement with the STEIPA formalism (figures 1 and 2), which takes into account only the triplet effective interactions corresponding to two consecutive nn pairs : the slight difference may be due to the fact that, in the present STEIPA results, not all triplet interactions were taken into account. More generally, one can see that the STEIPA results (or second step of the IM) achieve approximately half the 'distance' between PEIPA and DTEIPA results, the latter being considered as almost exact. The IM must naturally converge towards the DTEIPA results, which is shown in figure 2 for the extreme case of $\omega_B/\omega_A = 10^5$ (percolation threshold) : a quantitative

agreement is achieved for the step number 20 of the IM, whereas a qualitative behaviour is already observed by the fifth step, which would correspond to a five-site return path of the vacancy.

As a conclusion, there seems to be a direct link between the effective interactions used in the SCMF formalism and the actual return probability of a vacancy in the framework of the collective correlation effect : the PEIPA (respectively STEIPA) models describe a system included in an averaged one-component gas and restrict the correlation effects to the precise calculation of a single (respectively double) jump of the vacancy, plus an uncorrelated path through this average gas. The accuracy of this description decreases when the system becomes more correlated, i.e. when longer return paths of the vacancy must be taken into account. Particularly, the percolation limit is well described only with a decoupling scheme accounting for long-range paths. To further investigate the link between effective interactions and return paths, a computer-calculation of the n-point moments is required.

[Insert figure 1 about here]

[Insert figure 2 about here]

4.2 Interacting alloy

4.2.1. Existing models and simulations : In our knowledge there are three other models which account for short range interactions. First one is the Path Probability Method (PPM) [20, 21, 22] which was inspired by the Cluster Variation Method (CVM) developped for the calculation of thermodynamic quantities. First versions provide with a semi-analytical expression of the phenomenological coefficients of a multicomponent bcc alloy. The effect of surrounding is accounted for by means of interactions with nn atoms which are broken when the migrating atom exchanges position with a nn vacancy. Exchange frequencies are decomposed into a product of 'breaking bonds', each one

corresponding to a probability of forming a pair multiplied by an exponential of the nn interaction energy. The probability of a nn bond is then calculated using the pair approximation of the CVM. A satisfying agreement with Monte Carlo simulations was obtained as long as jump frequency ratios were not too high [20]. Within the same limitations of low correlation effects, the first version of the SCMF theory [25] as well as the recent formalism introduced by Qin, Allnatt and Allnatt [24] are to be cited. The latter leads to the Onsager matrix by calculating the two first moments of the time correlation function in a binary system, but no self-consistent scheme was introduced in the case of an interacting alloy : as a consequence it cannot predict a percolation limit, and its validity is limited to ratios of exchange frequencies near from unity. Moreover, for sake of complexity, it was derived only in the case of the simple cubic lattice, and was not extended to the tracer correlation factors.

Based on the same exchange frequency model, Stolwijk [23] could calculate the tracer correlation factors of a binary bcc alloy and for the first time included a self-consistent scheme together with the formalism of an interacting alloy. The derivation is mostly intuitive : it uses the breaking bonds introduced by Kikuchi and Sato and extends the random walk theories of Manning to calculate the probability of a tracer to come back to its position in competition with the nn of the vacancy. The additional idea in comparison to Manning [15] is to introduce new frequencies which account for the position of the tracer atom after a first jump and to assume that the escape probability of a vacancy after the first exchange depends on the chemical species of the tracer atom. The obtained self-consistent equations are numerically solved and the resulting correlation factors are compared to the PPM ones [20] and to Monte carlo simulations using the same atomic model.

The Stolwijk estimation agrees very well with Monte Carlo simulations whereas the PPM results are found to be quite different. The authors of the PPM method attributed the discrepancy to the fact that ensemble averages were used into the calculation although strong correlation effects like a percolation limit require to follow the motion of a small number of particles for a long time [21]. It is

then suggested to replace ensemble averages by time averages and to use a tagging process to follow an individual tracer atom. The time conversion consists then in tagging a tracer atom, replacing the ensemble averages concerning the other atoms by equilibrium time averages and following the ideas of Manning and Stolwijk to calculate the probability of an atom to exchange with a vacancy as a probability in competition with the jump back of the tracer atom which has just exchanged its position with the vacancy. This new PPM version applied to the calculation of correlation factors in a binary bcc alloy leads to a percolation limit. In the case of a bcc disordered alloy without interaction, this limit is found equal to $1/(z-1)$, or to $=(1-f_0)/(1+f_0)$ under their assumption that $f_0=(z-2)/z$ and is equivalent to a static calculation of the percolation limit using a pair approximation of the CVM. However the classic percolation limit obtained by the most accurate random lattice gas theories as well as our upgraded SCMF is $(1-f_0)$: **this value is satisfactorily close to the one obtained by Monte Carlo simulations [2, 3], although not strictly equal to the site percolation threshold of the considered cristallographic structure given by such simulations [39].**

Surprisingly, although the work of Sato and Kikuchi [21] was motivated by the results obtained by Manning and Stolwijk, there is no explicit comparison with those theories. Only values for an alloy without anti-symmetric term ($V_{AA}=V_{BB}$) are presented, for which Stolwijk's simulations showed no important correlation effects when the attempt frequencies are taken to be equal.

Eventually, one must consider the fact that no theory able to predict strong correlation effects like a percolation limit has actually solved the problem of collective correlation coefficients (i.e., the Onsager matrix) in a general interacting concentrated alloy **above the critical temperature**. Stolwijk [23] restricted his work to the tracer correlation coefficient, and Sato and Kikuchi, besides the tracer correlation coefficient [21], derived their latest model in terms of the L_{ij} only for the concentrated tracer case [22], which reduces to a non-interacting alloy. Because both theories use a

tagging procedure to follow individual trajectories of tracer atoms, they cannot easily be generalized to a calculation of collective correlation coefficients. As a conclusion the present SCMF upgrade is the only available theory which allows the calculation of all correlation coefficients in a multicomponent interacting alloy above its critical temperature including strong correlation effects like a percolation limit.

In terms of Monte Carlo simulations, the results of the DTEIPA approximation are tested against the simulations of Stolwijk for the tracer correlation factor, which best take into account the effects of thermodynamics in the alloy by using varying interaction energies for a same composition, as well as against the recent simulations performed in simple cubic lattices for the collective correlation factors [6, 34].

It is also to note that all these Monte Carlo simulations compute the transport coefficients in a system at equilibrium using the generalized Einstein relations : new Monte Carlo simulations were recently derived by Hartmann *et al.* [40] featuring a simulation box under a constant gradient of chemical potential, which allows to measure the transport coefficient in 'real' conditions : in most cases both methods appear to be equivalent if the gradient of chemical potential is not too high.

4.2.2. Results of the SCMF theory : In the SCMF theory, the correlation effects arise only from the ratio of the attempt frequencies of both species together with two energy differences : the ordering energy $V = (V_{AA} + V_{BB} - 2V_{AB})$ and the antisymmetric term $U = (V_{AA} - V_{BB})/V$. In the existing Monte Carlo simulations, the attempt frequencies are assumed to be equal. As a consequence, the correlation effects calculated by the SCMF model are the ones associated to the exchange frequency ratio :

$$\frac{\omega_B}{\omega_A} = exp\left(-\frac{\beta z V}{2}\left[(c_A - c_B) - (c_A + c_B)U\right]\right). \tag{55}$$

From a practical point of view, the results of the DTEIPA formalism in an interacting

alloy could have been obtained in a simple way by adding this atomic model to the previous MAA formalism. However, as the theoretical frame of the latter model is not consistent with the presence of thermodynamic interactions, the SCMF theory provides with a satisfactory theoretical basis for such a 'shortcut'. The corresponding Monte Carlo simulations represent a critical test of the SCMF theory since the exchange frequency ratio is not at all controlled by the attempt frequencies like in non-interacting systems, but only by the interaction energies. Besides, as the model is intended to deal with solid solutions without long range order, the product $\mid \beta V \mid$ should be inferior to the order-disorder transition value, which depends on the cristallographic structure.

Figures 3b and 3d show the predictions of the SCMF model (PEIPA and DTEIPA) compared with the Monte Carlo simulations by Stolwijk [23] in terms of tracer correlation coefficients in a bcc binary alloy. In both cases, the use of DTEIPA instead of PEIPA clearly improves the agreement between the SCMF model and the simulations. In the first case, the small change between PEIPA and DTEIPA means that the ratio of the exchange frequencies in this case is relatively near from unity (see figure 3a). Furthermore, in all cases, the agreement between SCMF and the MC simulations stays quantitative, or at least semi-quantitative for a temperature $T \geq 1.3T_c$. In the first two cases, the agreement can be said to be quantitative practically on the whole temperature range.

[Insert figure 3 about here]

However, although the DTEIPA improves the results of the SCMF in this case, the discrepancy with the simulations is still visible. This discrepancy may arise from the Bragg-Williams approximation used in the SCMF : when V/kT increases, the tendency to short range order is in contradiction with the point approximation. Thus it appears that, in the vicinity of the critical temperature, the correlation effects may be determined not only by the ratio of mean exchange frequencies, but involve also the variation of exchange frequencies upon the local environment of the exchanging pair

which is not explicitly taken into account by the present version of the SCMF theory. Eventually, if Stolwijk's model appears to be slightly more efficient, it must be noticed that the SCMF results achieve a better accuracy than the Kikuchi and Sato [20] model.

The same arguments can be used when comparing the SCMF results to the theory of Qin *et al.* [24] and Monte Carlo simulations [6, 34] in terms of collective correlation coefficients. Figures 4b and 4d show the factors f_{AA} and $f_{AB}^{(A)}$ in a simple cubic binary alloy with an ordering energy $V/kT = 0.63$ as a function of the composition of the alloy. Due to the jump frequency ratios (upper curves), the difference between the PEIPA and DTEIPA formalisms are always lower than 2% : as a consequence only the DTEIPA is represented. In both cases we observe a visible discrepancy between both theoretical models and the Monte Carlo simulations, while the results of the DTEIPA are very near from the theory of Qin *et al.*. As the mean jump frequency ratio does not play an important role, we expect that the limitations of both models concern the accounting of the local environment of the jumping species. In a simple cubic lattice, it is known that the point approximation has a low efficiency due to the low number of nn sites, which explains why the SCMF is less efficient than in a bcc alloy. However, unlike Stolwijk's model for the tracer diffusion, the method of Qin *et al.* to account for the local environment is not sufficient to reach a quantitative agreement with the Monte Carlo simulations, although it remains slightly better than the SCMF treated within the point approximation. We can note that in the limit of a dilute alloy, a recent upgrade of the SCMF theory [27] could ameliorate its results.

[Insert figure 4 about here]

Nevertheless, one advantage of the SCMF theory upon the models of Stolwijk [23] or Qin *et al.* [24] is its ability to calculate both tracer and collective correlation coefficients with a reasonable accuracy in interacting alloys. Figure 5 shows for example the four collective coefficients calculated for the same conditions as figures 3b and 3d. Coefficients f_{AA} and f_{BB} bear the same global behaviour as

the tracer coefficients f_A and f_B as expected, and the most important changes between the PEIPA and DTEIPA approximations concern the cross coefficients as well as the diagonal coefficient of the slowered atom, f_{BB}.

[Insert figure 5 about here]

In conclusion, the main limit of the SCMF model in the DTEIPA formalism remains the use of the point approximation, which can lead to a maximal error of about 25% in the calculation of the collective correlation coefficients in a simple cubic alloy, although this error is lower in other lattice structures like bcc. Consequently the next upgrade of this theory should be a more precise accounting of the local environment, following for example the route of Nastar [27] in the case of a dilute alloy.

5 Conclusion

We presented an upgrade of the SCMF theory which gives the transport coefficients of an interacting system with short range order from an atomic diffusion model including a thermodynamic description of the alloy. In the extreme case of a non-interacting system, our model reduces to the Moleko *et al.* [18] (MAA) formalism which is known to be in excellent agreement with Monte Carlo simulations. In interacting systems, a single effective jump frequency per species arises from the formalism as a function of the atomic interactions : this property allows to build predictive diffusion models accounting for the composition and temperature dependence of the jump frequencies and of the infered correlation effects. Although the agreement with Monte Carlo simulations is slightly poorer than earlier theories, principally due to the use of the point approximation, the upgraded SCMF theory is the only one which combines the prediction of a percolation limit as well as the calculation of the entire set of correlation coefficients in an interacting alloy **with short range order**. A new interpretation of the Moleko *et al.* decoupling scheme is also proposed in terms of an iterative

calculation of the correlation coefficients : the link with the return paths of the vacancy is now quantitatively established as a function of the length of these paths. Within the SCMF formalism it was recently shown that it is possible to introduce a better description of the short range order effects on the atom-vacancy exchange frequency [27]. Next challenge will be to incorporate these effects into the present SCMF version.

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Appendix A: Mean exchange frequency in the point approximation

In this section we show how the statistical point approximation in the SCMF formalism leads to the introduction of a single mean exchange frequency per atomic species. Let us consider the equilibrium two-point moment defined by :

$$\langle n_i^\alpha n_j^\beta \rangle^{(0)} = \sum_{\mathbf{n}} n_i^\alpha n_j^\beta P_0(\mathbf{n}), \tag{56}$$

At equilibrium this quantity is assumed to obey the point approximation (equation (11)).

Let us consider the one-point moment $\langle n_i^\alpha \rangle^{(0)}$. We introduce the function $\hat{G} = \ln \hat{P}_0$. As $\hat{G}$ is a polynomial function of the occupation numbers and using equation (21), one can write :

$$\begin{aligned} \langle n_i^\alpha \rangle^{(0)} &= \sum_{\mathbf{n}} n_i^\alpha \exp\left[\hat{G}(n_i^\alpha = 1)\right] \\ &= \sum_{\mathbf{n}} n_i^\alpha \exp\left[\frac{\partial \hat{G}}{\partial n_i^\alpha} + \hat{G}(n_i^\alpha = 0)\right] \\ &= \sum_{\mathbf{n}} n_i^\alpha \exp\left(\hat{G}_i^\alpha + \hat{G} - \hat{G}_i\right), \end{aligned} \tag{57}$$

where $\hat{G}_i^\alpha$ is the derivative of $\hat{G}$ with respect to the occupation number n_i^α, and we have introduced $\hat{G}_i = \sum_A \hat{G}_i^A n_i^A$: $\hat{G} - \hat{G}_i$ is the contribution to $\hat{G}$ which does not involve the occupation numbers of site i, and $\hat{G}_i^\alpha$ is the contribution to $\hat{G}$ fulfilling the condition $n_i^\alpha = 1$. From equation (57) and the definition of P_0 (equation (2)) it is straightforward to derive the relation :

$$\langle n_j^\alpha \rangle^{(0)} = \langle n_j^v \exp[\beta(\mu_\alpha - \hat{H}_j^\alpha + \hat{H}_j^v)] \rangle^{(0)}. \tag{58}$$

It leads to the expression of the chemical potential :

$$\exp(\beta\mu_\alpha) = \frac{c_\alpha}{c_v} + \sum_{A,j} c_A (V_{ij}^{\alpha A} - V_{ij}^{vA}). \tag{59}$$

Such a transformation applied to a two-point average introduces second order derivatives of the Hamiltonian which represent the coupling between both sites :

$$\langle n_i^\alpha n_j^\beta \rangle^{(0)} = \langle n_i^\alpha n_j^v \exp[\beta(\mu_\beta - \hat{H}_j^\beta + \hat{H}_{jj}^\beta - \hat{H}_{ji}^{\beta\alpha} + \hat{H}_j^v - \hat{H}_{ji}^v + \hat{H}_{ji}^{v\alpha})] \rangle^{(0)}, \tag{60}$$

where $\hat{H}_{ji}^{\beta\alpha}$ is the second derivative of $\hat{H}$ with respect to n_i^α and n_j^β and $\hat{H}_{ji}^{\beta} = \sum_A \hat{H}_{ji}^{\beta A} n_i^A$.

However a point approximation is equivalent to neglect those correlations between sites, since equation (60) must be equal to the product of point averages which means a neglect of the second partial derivatives and a separation of the average into two terms :

$$\begin{aligned} \langle n_i^\alpha n_j^\beta \rangle^{(0)} &= \langle n_i^\alpha \rangle^{(0)} \langle n_j^v \exp[\beta(\mu_\beta - \hat{H}_j^\beta + \hat{H}_j^v)] \rangle^{(0)} \\ &= \langle n_i^\alpha \rangle^{(0)} \langle n_j^\beta \rangle^{(0)}. \end{aligned} \tag{61}$$

We apply the same approximation to the saddle point energies normalized by temperature, which converge to zero at high temperature like thermodynamic interactions. One has to note that such a decoupling procedure is not applied to the effective Hamiltonian : a reason is that h normalized by the temperature does not converge to zero at high temperature : for example the migration of atoms in a pure metal at infinite temperature will not be random while all the energy couplings are to be neglected, the kinetic couplings due to the vacancy mechanism being still present.

One eventually calculates the average in equation (12) as :

$$\begin{aligned} \langle n_i^\alpha n_j^v \widehat{w}_{ij}^{\alpha v} \rangle &= \langle n_i^\alpha n_j^v \gamma_{ij} \nu_\alpha \exp[-\beta(\sum_{\beta,k\neq i,j} V_{(s)k}^{\alpha\beta} - H_i^\alpha - H_j^v + H_{ij}^{\alpha v})] \rangle^{(0)} \\ &= \langle n_i^v n_j^v \exp[\beta(\mu_\alpha - H_i^\alpha + H_i^v)] \gamma_{ij} \nu_\alpha \exp[-\beta(\sum_{\beta,k\neq i,j} V_{(s)k}^{\alpha\beta} - H_i^\alpha - H_j^v + H_{ij}^{\alpha v})] \rangle^{(0)} \\ &= \gamma_{ij} \nu_\alpha \exp(-\beta\mu_\alpha) \langle \exp[-\beta(\sum_{\beta,k\neq i,j} V_{(s)k}^{\alpha\beta} - 2H_j^v + H_{ij}^{\alpha v})] \rangle^{(0)} \langle n_i^v n_j^v \rangle^{(0)} \\ &= \gamma_{ij} \omega_\alpha \frac{c_\alpha}{c_v} \langle n_i^v n_j^v \rangle^{(0)}, \end{aligned} \tag{62}$$

If the interactions at substitutional and saddle point positions are restricted to nn sites, respectively V_{AB} and $V_{AB}^{(s)}$ the final expression for the mean exchange frequency ω_α states :

$$\omega_\alpha = \nu_\alpha \exp\left[-\frac{\sum_A (z' V_{\alpha A}^{(s)} - z V_{\alpha A} - z V_{vA}) c_A}{kT}. \right] \tag{63}$$

Note that within a point approximation the number of substitutional atomic interactions to break during one jump is equal to z, whereas before the average procedure the jumping atom has $z-1$

atoms and one vacancy as nearest neighbours.

Appendix B: n-point moments out of equilibrium

The effective interactions represent the correlation effect contribution to the transport coefficients, but they are also involved in the calculation of the non-equilirbium n-point moments of a system under a gradient of chemical potential. In particular, the decoupling relations between pair and triplet effective interactions which were postulated in section 3.3 can also be taken as a closure relationship beween 3-point and 2-point moments. Indeed, although equation (40) has proven to be very accurate, no simple physical meaning has been attached to it so far in its original context (Moleko *et al.* [18] formalism). We now examine the same relationship in terms of the n-point moments. Instead of calulating the time derivative of the n-point moments, which leads to the transport coefficients, we now focus on the value of those moments. The superscript $\langle\rangle^{(0)}$ stands for an equilibrium thermodynamic average (we will also note $c_A = \langle n_i^A \rangle^{(0)}$) : when it is not present, the average is processed out of equilibrium.

Using equation (21), it is straightforward to establish the expression of the first n-point moments, to first order in the effective interactions :

$$\langle n_i^A \rangle = \langle n_i^A \rangle^{(0)} (1 - \delta\mu_i^A - h_i^A), \tag{64}$$

$$\langle n_i^A n_j^B \rangle = \langle n_i^A \rangle \langle n_j^B \rangle (1 + h_{ij}^A + h_{ji}^B - h_{ij}^{AB} - \sum_{\sigma,\sigma'} h_{ij}^{\sigma\sigma'} c_\sigma c_{\sigma'}), \tag{65}$$

$$\begin{aligned} \langle n_i^A n_j^B n_k^C \rangle = {} & \langle n_i^A \rangle \langle n_j^B \rangle \langle n_k^C \rangle (1 + h_{ij}^A + h_{ji}^B - h_{ij}^{AB} - \sum_{\sigma,\sigma'} h_{ij}^{\sigma\sigma'} c_\sigma c_{\sigma'} \\ & + h_{ik}^A + h_{ki}^C - h_{ik}^{AC} - \sum_{\sigma,\sigma'} h_{ik}^{\sigma\sigma'} c_\sigma c_{\sigma'} \\ & + h_{kj}^C + h_{jk}^B - h_{kj}^{CB} - \sum_{\sigma,\sigma'} h_{kj}^{\sigma\sigma'} c_\sigma c_{\sigma'} \\ & + h_{ijk}^{AB} + h_{ikj}^{AC} + h_{jki}^{BC} - \sum_{\sigma,\sigma',\sigma''} h_{ijk}^{\sigma\sigma'\sigma''} c_\sigma c_{\sigma'} c_{\sigma''}). \end{aligned} \tag{66}$$

Remembering that the effective interactions involving vacancies are set to zero, we make appear

equation (40) when defining the following sum S_{AB} of 3-point moments :

$$\begin{aligned} S_{AB} &= (\langle n_i^A n_j^B n_k^V\rangle - \langle n_i^A n_j^V n_k^B\rangle) - (\langle n_j^A n_i^B n_k^V\rangle - \langle n_j^A n_i^V n_k^B\rangle) + (\langle n_k^A n_i^B n_j^V\rangle - \langle n_k^A n_i^V n_j^B\rangle) \\ &= \langle n_i^A\rangle(\langle n_j^B\rangle\langle n_k^V\rangle - \langle n_k^B\rangle\langle n_j^V\rangle) - \langle n_j^A\rangle(\langle n_i^B\rangle\langle n_k^V\rangle - \langle n_k^B\rangle\langle n_i^V\rangle) + \langle n_k^A\rangle(\langle n_i^B\rangle\langle n_j^V\rangle - \langle n_j^B\rangle\langle n_i^V\rangle) \\ &\quad + c_A c_B c_V[(h_{ijk}^{AB} - h_{ikj}^{AB}) - (h_{jik}^{AB} - h_{jki}^{AB}) + (h_{kij}^{AB} - h_{kji}^{AB})], \end{aligned} \tag{67}$$

where the last terms can be transformed using the decoupling relation (40) : for example, one can change $h_{ijk}^{AB} - h_{jik}^{AB}$ into $\sum_\sigma(\delta_{B\sigma} - f_{B\sigma}^{(B)})(h_{jk}^{\sigma_A} - h_{ik}^{\sigma_A})$. Eventually, the sum of S_{AB} over all chemical species A gives rise to the following relation :

$$\Delta K_{ij}^{BV} + \Delta K_{jk}^{BV} - \Delta K_{ik}^{BV} = \sum_\sigma(\delta_{B\sigma} - f_{B\sigma}^{(B)})(\Delta K_{ij}^{\sigma V} + \Delta K_{jk}^{\sigma V} - \Delta K_{ik}^{\sigma V}), \tag{68}$$

where we have introduced the correlator

$$\Delta K_{ij}^{BV} = \frac{\langle(n_i^B - \langle n_i^B\rangle)n_j^V\rangle - \langle(n_j^B - \langle n_j^B\rangle)n_i^V\rangle}{c_B c_V}. \tag{69}$$

For a multicomponent alloy with N species, this set of relations forms a linear system of equations between the quantities $\tilde{K}_{ijk}^\sigma = \Delta K_{ij}^{\sigma V} + \Delta K_{jk}^{\sigma V} - \Delta K_{ik}^{\sigma V}$, namely :

$$\mathbf{f}.\tilde{\mathbf{K}} = \mathbf{0}, \tag{70}$$

where $\mathbf{f}$ is the matrix of the correlation coefficients and $\tilde{\mathbf{K}}$ is a column matrix. The determinant of the $\mathbf{f}$ matrix is non-zero in every case where we have analytical or numerical results in the SCMF DTEIPA formalism. Thus, we arrive at the simple conclusion :

$$\Delta K_{ij}^{\sigma V} + \Delta K_{jk}^{\sigma V} - \Delta K_{ik}^{\sigma V} = 0 \tag{71}$$

for all species σ. This result seems to be due to the use of the Moleko *et al.* decoupling scheme which gives rise to a simplified relationship between the correlators ΔK. As equation (71) is also true in the PEIPA approximation but not in the STEIPA formalism, we can infer that the decoupling scheme is a mean to insure this relation.

Figure 1 : Correlation factor f_{BB} as a function of composition in a bcc solid solution AB for two different mean exchange frequency ratios $w_B/w_A = 10$ or 100. Solid lines refer to a truncation to pair effective interactions, dashed lines to a truncation to the first shell 3-body effective interactions (compact triangles) in the STEIPA approximation, dotted lines to the second step of the Iterative Method (IM) and bold lines to the converged DTEIPA formalism. The results of the DTEIPA and of the MAA formalisms [18] are strictly equal.

Figure 2 : Correlation factor f_{BB} as a function of composition in a bcc solid solution AB for a mean exchange frequency ratio $w_B/w_A = 10^5$. Solid line refers to a truncation to pair effective interactions, dashed line to a truncation to the first shell 3-body effective interactions (compact triangles) in the STEIPA approximation, dotted lines to the steps 2, 3, 5 and 20 (from top to bottom) of the Iterative Method and bold line to the converged DTEIPA formalism.

Figure 3 : Tracer correlation factor f_A and f_B in a bcc alloy $A_{0.5}B_{0.5}$ with ordering tendency as a function of the ordering energy V normalized by kT. The antisymmetric term U is equal to -0.6 (a and c) or to -1.2 (b and d). Bold solid lines refer to the Monte Carlo simulations by Stolwijk [23], which coincide with his theory, bold dashed lines to the model of Kikuchi and Sato [20]. The SCMF results correspond to the thin solid lines (DTEIPA) and dotted lines (PEIPA). The upper curves show the ratio ω_B/ω_A as calculated by the SCMF theory in the point approximation (equation (55)).

Figure 4 : Collective correlation factors f_{AA} and $f_{AB}^{(A)}$ in a simple cubic binary alloy with ordering tendency as a function of the concentration $C(A)$ for an ordering energy $V/kT = 0.63$. The antisymmetric term is equal to zero (a and c) or 0.5 (b and d). Square symbols refer to the Monte Carlo calculations by Zhang *et al.* [34] and Qin and Murch [6], dotted lines to the model of Qin *et al.* [24] and solid lines to the SCMF theory in the DTEIPA approximation. The upper

curves show the ratio ω_B/ω_A as calculated by the SCMF theory in the point approximation (equation (55)).

Figure 5 : Collective correlation factors calculated by the SCMF theory in a bcc alloy $A_{0.5}B_{0.5}$ with ordering tendency as a function of the ordering energy V normalized by kT. The antisymmetric term U is equal to -1.2. Dotted lines refer to the PEIPA approximation, solid lines to the DPEIPA.

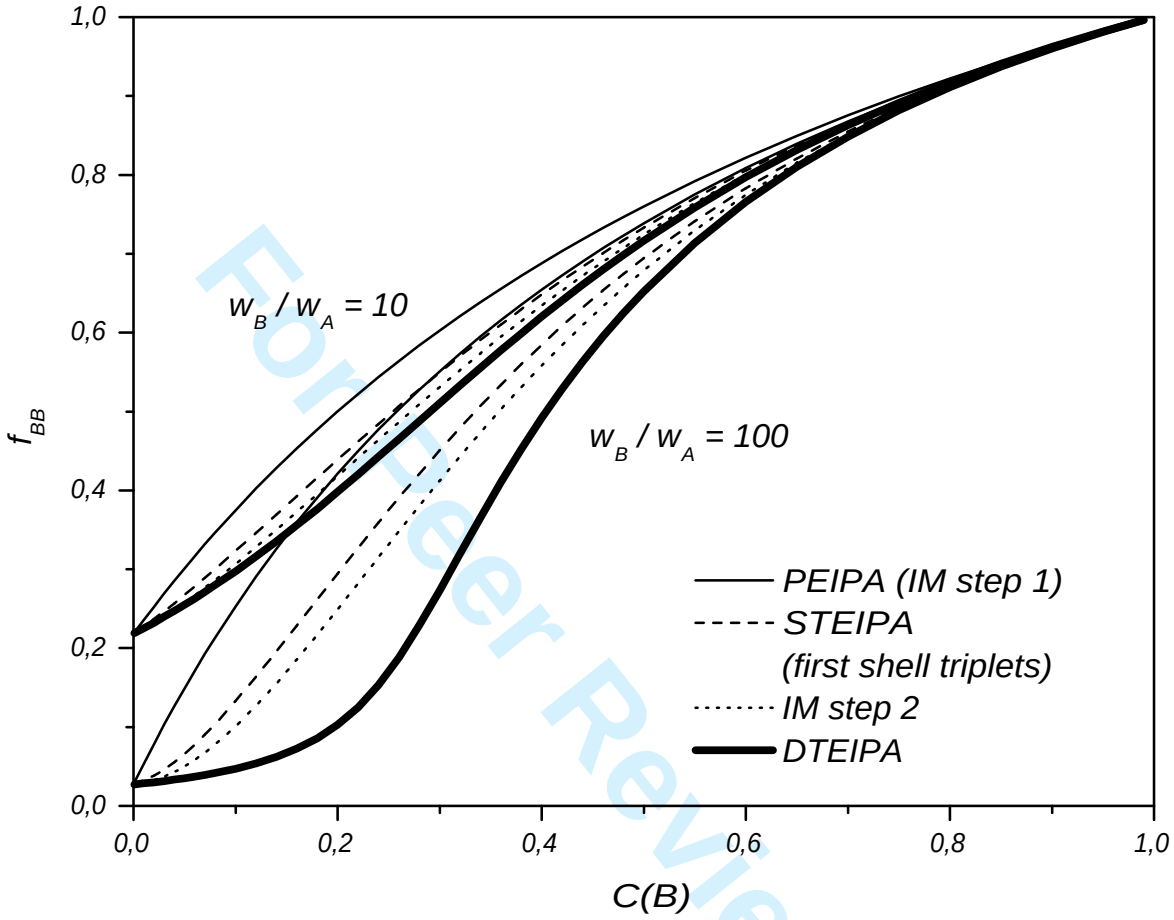
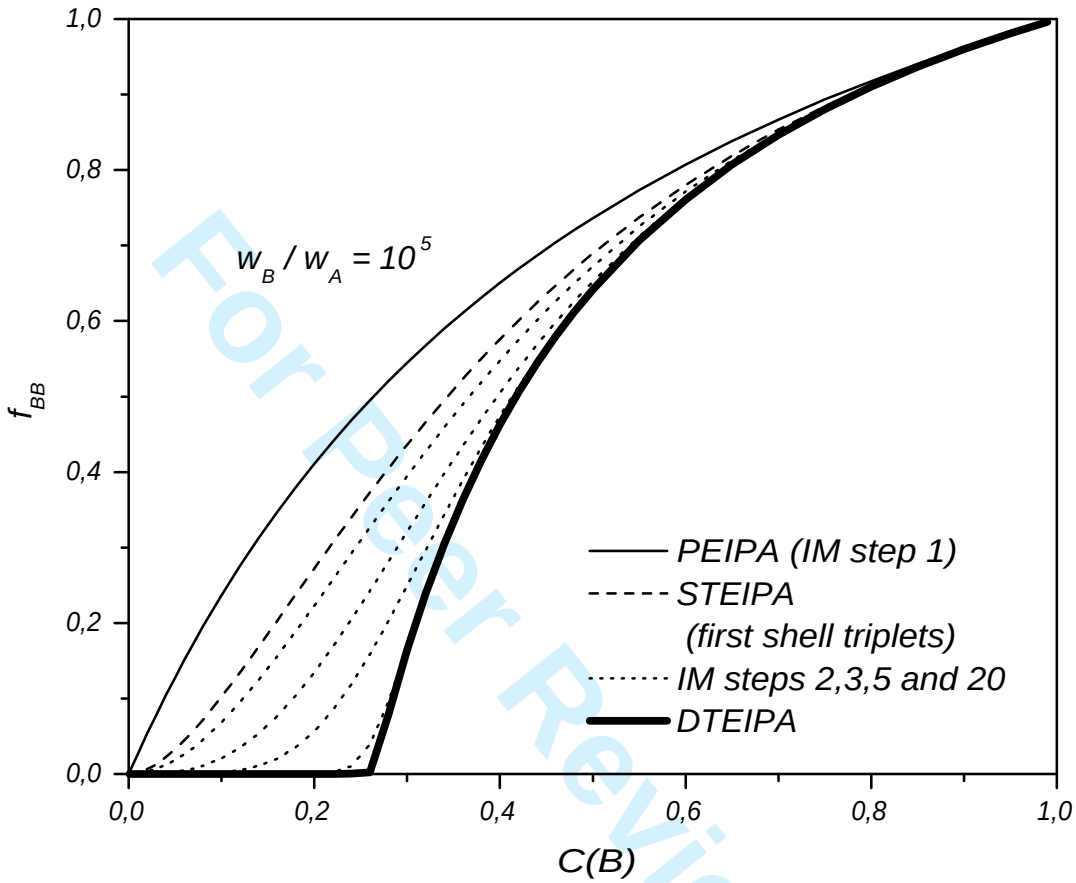


Figure 1:



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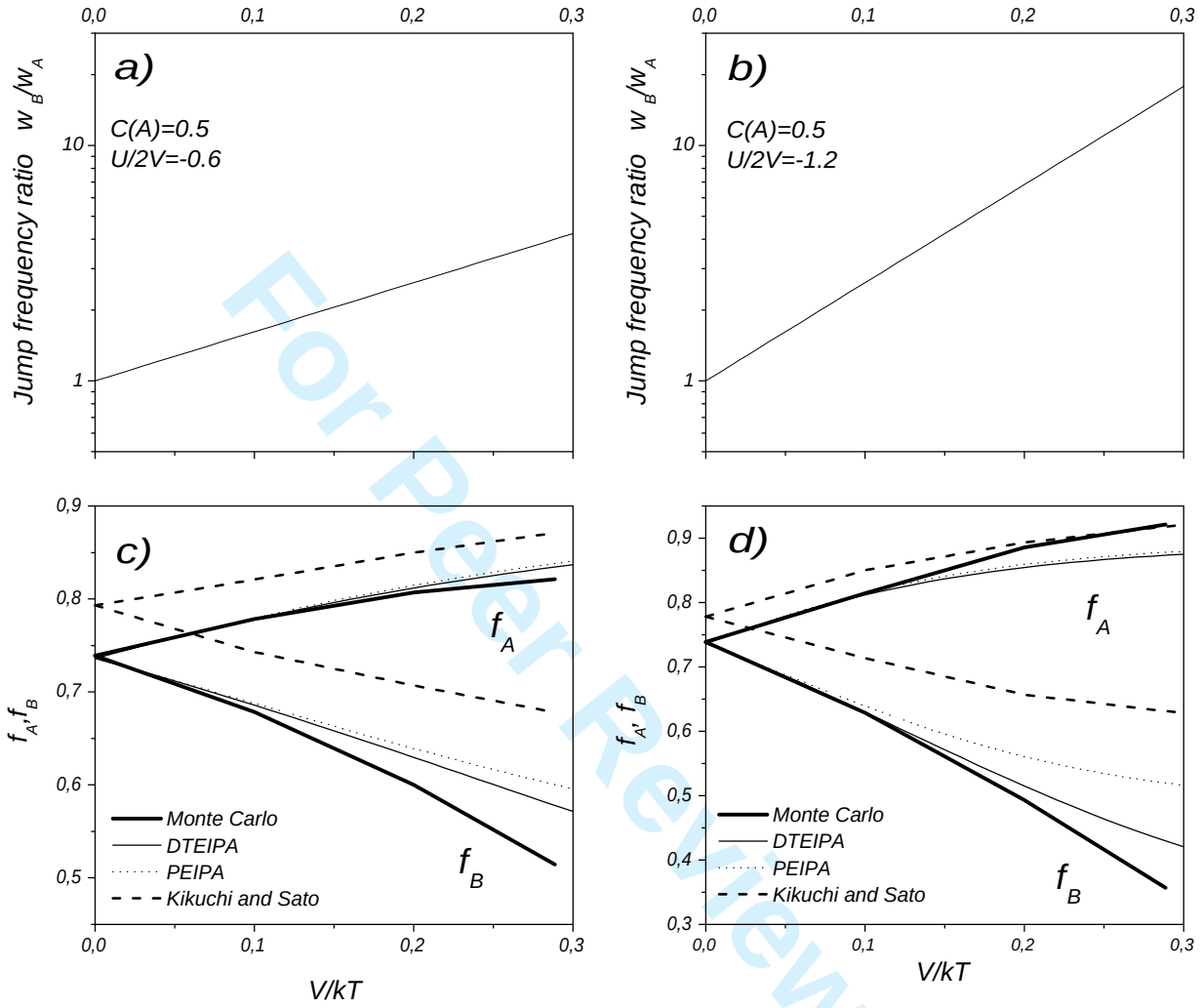

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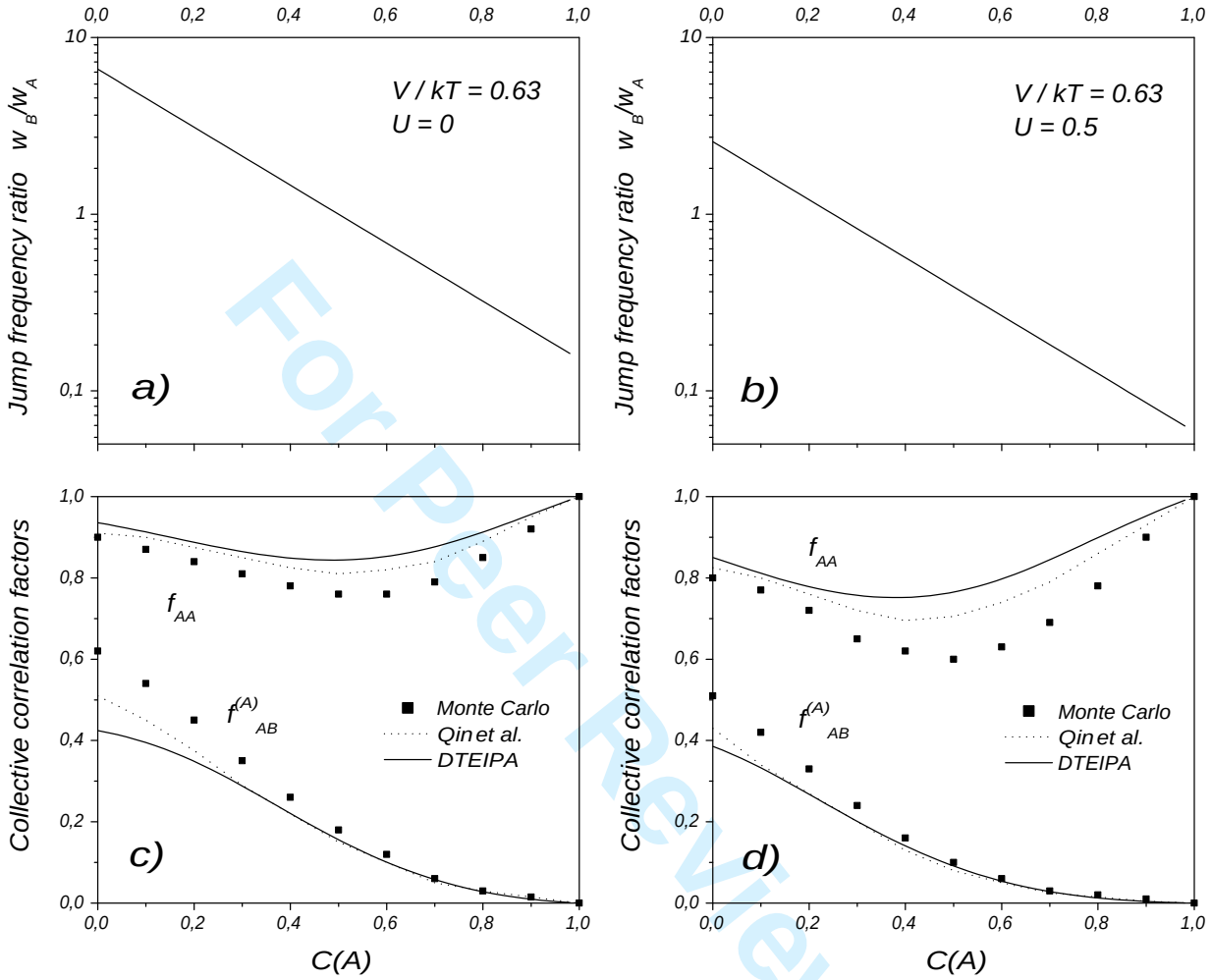

Figure 4:

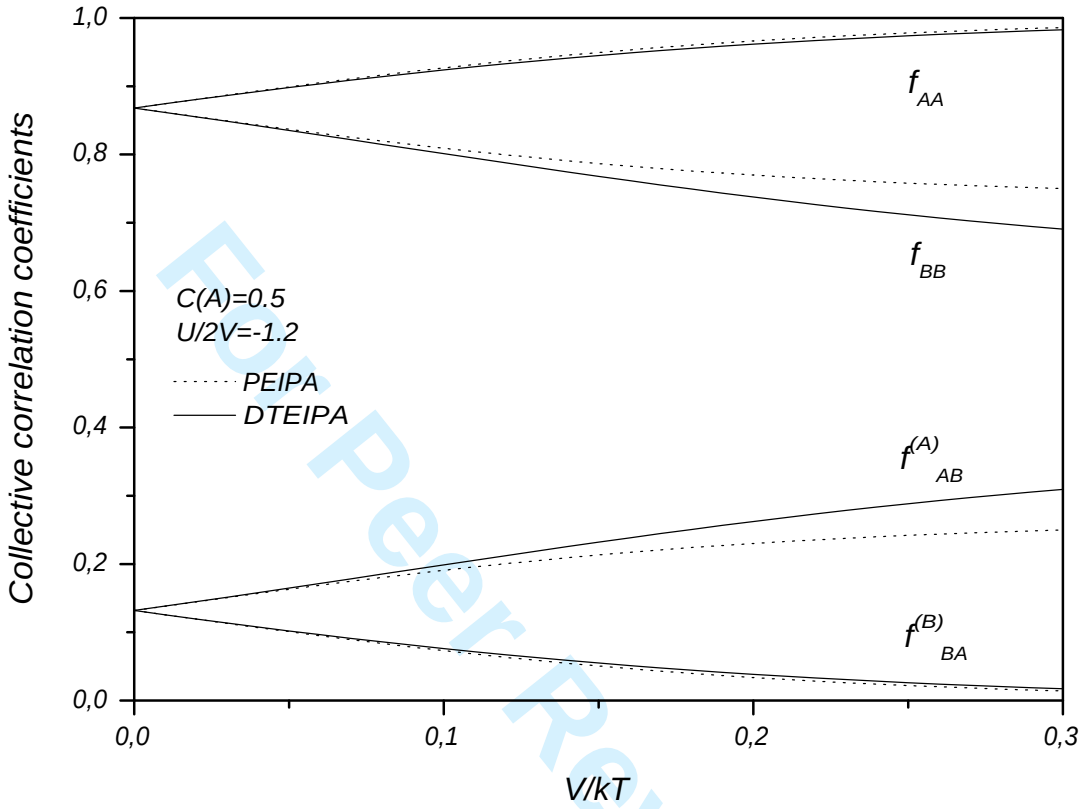

Figure 5: